(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 964 031 B1

(12) EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention of the grant of the patent:
07.04.2004 Bulletin 2004/15

(51) Int Cl.⁷: **C08L 67/02**, C08J 5/18, B65D 1/00 // (C08L67/02, 77:06)

(21) Application number: **99109316.2**

(22) Date of filing: **28.05.1999**

(54) Polyester resin blends with high-level gas barrier properties

Polyesterabmischungen mit guten Gasbarriereeigenschaften

Compositions à base de polyester avec de bonnes propriétés de barrière au gaz

(84) Designated Contracting States:
AT BE CH DE DK ES FI FR GB IT LI NL PT SE

(30) Priority: **11.06.1998 IT MI981335**

(43) Date of publication of application:
15.12.1999 Bulletin 1999/50

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(56) References cited:
EP-A- 0 092 979
EP-A- 0 752 437
EP-A- 0 819 728
WO-A-93/20147
WO-A-94/09069
US-A- 4 837 115
US-A- 5 281 360

- **CHEMICAL ABSTRACTS, vol. 113, no. 25, 17 December 1990 (1990-12-17) Columbus, Ohio, US; abstract no. 232752, XP002126791 & JP 01 272660 A (UBE IND., LTD.) 31 October 1989 (1989-10-31)**
- **DATABASE WPI Section Ch, Week 198603 Derwent Publications Ltd., London, GB; Class A23, AN 1986-017548 XP002126792 & JP 60 240452 A (MITSUI PETROCHEM IND CO LTD), 29 November 1985 (1985-11-29)**

EP 0 964 031 B1

Description

[0001] The present invention relates to biaxially-oriented films and containers provided with high resistance to gas permeability, and to the polymeric materials used to prepare said containers and films.

[0002] Aromatic polyester resins are used in ever-increasing amounts in the production of beverage containers and films.

[0003] The barrier properties of aromatic polyester resins are rather limited. In the case of containers for carbonated beverages prepared from said resins, the possibility to preserve the beverages for a sufficiently long time is uncertain.

[0004] Polyamide resins have remarkable mechanical properties, but they have the drawback that they have a high moisture absorption which reduces their properties.

[0005] Polyamide resins are normally used mixed with aromatic polyester resins in order to improve the mechanical characteristics of the latter. The presence of polyester resin in the mix reduces the moisture-absorbing tendency of polyamide resins.

[0006] Mixing the resins, however, is difficult because of their poor compatibility in the melted state.

[0007] In order to obtain better mechanical properties and to avoid peeling in products, it has been suggested to mix the resins in the extruder in the presence of a dianhydride of a tetracarboxylic acid (JP 1-272660 Kokai).

[0008] Pyromellitic anhydride is the preferred compound.

[0009] The mechanical properties of the resulting mixtures can be improved further by subjecting the mixtures to a solid-state polycondensation treatment (WO 94/09069).

[0010] Among polyamides, the most commonly used polyamides, such as nylon 6 and 66, have slightly better gas barrier properties than polyester resins such as polyethylene terephthalate (PET) and copolyethylene terephthalates containing small proportions of units derived from isophthalic acid.

[0011] However, a polyamide obtained from m-xylylene diamine and adipic acid (poly-m-xylylene adipamide, poly MXD-6) is known as having considerable gas barrier properties (in relation to oxygen and carbon dioxide) which are distinctly better than those of polyethylene terephthalate.

[0012] This polyamide is used in mixture (obtained in an extruder) with PET or COPET in order to improve their barrier properties.

[0013] The oxygen permeability of a 1.5-liter PET bottle (produced by injection blow-molding) is reduced by approximately 50% when the bottle is obtained from a mixture which contains 16% by weight of polyamide and by approximately 20% when it contains 7% polyamide by weight.

[0014] The barrier properties of the 16% polyamide mixture are similar to those of a bottle formed of a two-layer film, one layer being PET and the other one being polyamide.

WO 93 20147 A discloses a polyester composition comprising 98.0 - 0.95 weight percent of a polyester and from 2 to 0.05 weight percent of a polyamide. Among other polyamides, poly-m-xylyleneamide is mentioned.

[0015] US-A-4 837 115 discloses a thermoplastic polyester composition comprising a thermoplastic polyester and a thermoplastic polyamide. Poly-m-xylyleneadipamide is mentioned among other polyamides.

[0016] It has now been found unexpectedly that it is possible to remarkably improve the barrier properties of biaxially-oriented films and containers which can be obtained from polyester resins used in a mixture with a polyamide such as poly MXD-6 if the polyester resin is first mixed in the melted state with a dianhydride of a tetracarboxylic acid and the resulting mixture is further mixed, again in the melted state, with a polyamide such as poly MXD-6, working under temperature and shear forces conditions and with viscosities of the melted polymeric components such as to render the polymeric components of the mixture compatible from the rheological viewpoint. The dianhydride is mixed with the polyester resin in an amount from 0.01 to 3% by weight.

[0017] Pyromellitic dianhydride is preferred. Other dianhydrides that can be used are dianhydrides of 1, 2, 3, 4-cyclobutane tetracarboxylic acid, 3,3':4,4'-benzophenone tetracarboxylic acid, 2,2 bis-(2,4-dicarboxyphenyl)ether. The dianhydrides of aromatic tetracarboxylic acids are preferred.

[0018] Preferably, the polyester resin is a copolyethylene terephthalate in which up to 25%, preferably 1 to 15%, of the units derived from terephthalic acid are substituted by units or sequences derived from isophthalic acid or from mixtures thereof with naphthalene dicarboxylic acids.

[0019] The polyamide is preferably poly MXD-6. Other polyamides that can be used are those obtainable from an aliphatic dicarboxylic acid other than adipic acid containing 6 to 22 atoms of carbon and an arilene diamine, preferably m-xylylene diamine.

[0020] Said dicarboxylic acid is preferably suberic, sebacic and dodecanoic acid.

[0021] Polyamides with crystallization rates similar to those of polyester are preferably used.

[0022] The numeral molecular weight of the starting polyamide is generally between 8000 and 50000.

[0023] The terminal-NH_2 groups of the starting polyamide can be reacted with epoxy compounds in order to increase its dispersion in the polyester matrix. Epikote from the Shell Italia is an example of usable epoxi compounds.

[0024] Preferably, the polyamide is used in an amount equal to 5 to 30% by weight on the mixture. Larger amounts

can be used depending on the final properties of the mixture.

[0025] It is in fact possible, and it is another aspect of the invention, to prepare, operating according to the method of the invention, mixtures having a polyamide content of more than 50% by weight and up to 80-90% by weight which can be used as master batch.

[0026] A preferred mixing process consists in extruding the polyester resin with the addition of the dianhydride and in subsequently extruding the mixture with the addition of the polyamide.

[0027] It is possible to work in a single stage by premixing in the extruder the polyester and dianhydride first and then adding the polyamide in the extruder.

[0028] In order to achieve good compatibilization among the polymeric components, their viscosities in the melted state has to be very similar.

[0029] Preferably, the ratio between the viscosity of the polyester and the viscosity of the polyamide is between 0.2:1 and 4:1.

[0030] Operating under the above conditions it is possible to obtain compositions wherein the polyamide is dispersed in the polyester matrix with domains having size of less than 1 micron, preferably in the range from 0:2 to 0.4 micron. The microstructure was obtained by scanning electron microscope (S.E.M.) of the fracture surface of injection molded small bars treated with formic acid to extract the polyamide. The bars obtained according to example 1 have a microstructure wherein the dispersed phase has a size of less than 0.5 micron. The size of the domains in the bars obtained from example 1 but without using PMDA are higher than 1.5 micron as average. The microstructure according to the invention is characteristic in particular of the blends of poly MXD-6 with PET or copolyethylene thereftalates containing up to 25% of units deriving from isophtalic acid.

[0031] It is surprising that when working under the mixing conditions according to the invention it is possible to obtain materials having gas barrier properties (relative to O_2 and CO_2) which are far higher than those obtainable by mixing the polyester resin and the polyamide in the absence of the dianhydride of tetracarboxylic acid or by mixing the three components of the mixture simultaneously or by first mixing the polyamide with the dianhydride and then adding the polyester resin.

[0032] Oxygen permeability in 1.5-liter bottles with an average thickness of 225 microns can be reduced of 4 or more times and CO_2 permeability can be reduced by 2 or more times as a function of the content of the polyamide (pMXD-6).

[0033] The polyester resin is obtained by polycondensation (according to known methods) of terephthalic acid or lower diesters thereof with a diol with 2-12 carbon atoms, such as for example ethylene glycol, 1,4-butanediol and 1,4-cyclohexane dimethylol. The copolyethylene terephthalate is, as mentioned, the preferred resin for preparing containers.

[0034] The polyethylene terephthalate homopolymer can be conveniently used in the preparation of biaxially-oriented films.

[0035] The starting polyester resin used in the preparation of the compositions according to the invention has an intrinsic viscosity of 0.3 to 0.8 dl/g. The initial viscosity can be increased by subjecting the resin, premixed with the dianhydride of the tetracarboxylic acid or the mixture containing the polyester resin, the polyamide and the dianhydride, to a solid-state polycondensation treatment at temperatures between approximately 150 and 230°C for a time and at temperature conditions sufficient to increase by at least 0.1 units the viscosity of the polyester resin.

[0036] Since the polyester resin is difficult to separate by solvent extraction in the mixture, the increase in intrinsic viscosity of the polyester resin in the mixture is considered similar to the increase in the polyester resin when it is treated alone in the same temperature and duration conditions to which the mixture has been subjected.

[0037] The solid-state polycondensation treatment, in addition to leading to an increase in the intrinsic viscosity of the polyester resin, allows to improve the mechanical properties of the compositions, particularly impact resistance.

[0038] The treatment applied to the polyester resin added of the dianhydride of the tetracarboxylic acid allows to bring the viscosity of the resin in the melted state to values which are similar to those of the polyamide resin, particularly when the initial polyester resin has relatively low intrinsic viscosity values.

[0039] The mixing of the polyester with the dianhydride and then with the polyamide is performed in a single- or twin-screw extruder. Contrarotating and intermeshing twin-screw extruders are preferred, using residence times of generally less than 180 seconds and working at temperatures above the melting temperatures of the polymeric components, generally between 200° and 300°C.

[0040] The biaxially oriented films and containers are prepared according to known methods. For example, bottles for beverages are prepared by injection-stretch blow molding; biaxially oriented films are prepared with the double-bubble method or by cast-extrusion followed by biaxial stretching.

[0041] The material according to the invention can also be used to prepare multilayer films comprising, as a core layer, a biaxially oriented film obtained from the material according to the invention.

[0042] Another application of the blends according to the invention, wherein the polyester resin is a copolyethylene therephthalate with 10% or more of units from isophthalic acid resides in the preparation by free blowing of preforms of high capacity pouches (5 l. or more) suitable for being filled with liquids such as soft drinks or others.

[0043] The pouches have high clarity and good mechanical properties. They can be easily folded without breakage or stress withening problems.
[0044] The intrinsic viscosity is measured in solutions of 0.5 g of resin in 100 ml of 60/40 solution by weight of phenol and tetrachloroethane, at 25°C according to ASTM standard D 4603-86.
[0045] The measurement of the melt viscosity is performed with a Goettfert rheometer equipped with a 2-mm capillary tube, working at 280°C with a shear rate of 100 sec^{-1}.

EXAMPLES

[0046] The following examples are given to illustrate but not to limit the invention.

EXAMPLE 1

[0047] 20 kg/h of crystallized granules of copolyethylene terephthalate (COPET) containing 4.5% isophthalic acid (IPA) with IV = 0.6 dl/g (predried at 140°C in vacuum for at least 12 h) are fed together with 20 g/h of pyromellitic dianhydride (PMDA) (0.1% by weight on the COPET) in a twin-screw extruder with contrarotating and intermeshing screws and then pelletized.
[0048] The operating conditions are:

Screw rotation rate: 100 rpm
Cylinder temperature: 280°C throughout the cylinder
COPET feed: 20 kg/h
PMDA feed: 20 g/h
Residence time: 1.5 min

[0049] The resulting pellets were crystallized at 130°C in a reactor in continuous under nitrogen flow.
[0050] IV after extrusion was 0.61 dl/g.
[0051] 20 kg/h of crystallized COPET containing 0.1% PMDA obtained as mentioned above are fed into a twin-screw extruder provided with contrarotating and intermeshing screws together with 2.2 kg/h of poly-MXD-6 (Mitsubishi Gas Chemical - MGC - Japan) having a viscosity in the molten state at 280°C and 100 sec^{-1} of shear rate of 1000 PAS and pelletized.
[0052] The conditions for preparing the mixture are the same used for the treatment of COPET with the addition of PMDA.

EXAMPLE 2

[0053] Preparation of the mixture of COPET and PMDA of example 1 is repeated, the only difference being that COPET with 4.5% isophthalic acid is replaced with a mixture containing 92/8 by weight of COPET with 2% isophthalic acid, IV = 0.8 dl/g and 8% polyethylene isophthalate.
[0054] The IV of the pellets was 0.81 dl/g. The pellets are crystallized at 130°C in a reactor operating continuously in nitrogen.
[0055] The pellets are then extruded together with 10% by weight of poly MXD-6 in the conditions of example 1.

EXAMPLE 3

[0056] The preparation of example 1 (premixing of COPET with PMDA and subsequent extrusion with 10% poly MXD-6) was repeated, with the only difference that the COPET used contained 2% isophthalic acid and had an IV of 0.6 dl/g.

EXAMPLE 4

[0057] The preparation of example 1 was repeated, with the only difference that the mixture contained 70% by weight of poly-MXD-6.

EXAMPLE 5

[0058] A composition, prepared according to example 1, by using in place of COPET containing 4.5% IPA a mixture containing 86% by weight of COPET with 2% of IPA (IV = 0.8 dl/g) and 14% of polyethylene isophthalate, and in which

the percentage of poly-MXD was 7.5% by weight, was used to prepare 40 g preforms.

[0059] The preforms were submitted to free blowing using a Sidel machine equipped with an infrared heater to heat the preforms to 110°. The preforms were blown using air at 3 bar pressure. The obtained pouches have a capacity of 5 l. and are highly clear. They can be folded (when empty) and refilled with liquids.

[0060] The pouches filled with 51. water can withstand a drop impact of 1 m.

EXAMPLES 6,7

[0061] The mixtures obtained according to examples 1-4 were used to produce 36-g preforms using a Husky injection unit.

[0062] The preforms were then blown in a 1.5- and 2-liter cavity to produce bottles by stretch-blow molding. The thickness of the 1.5-liter bottles was 225 microns (average value) and the thickness of the 2-liter bottles was 195 microns (average value).

[0063] The permeability characteristics of the bottles with respect to O_2 and CO_2 are listed in table 1. Gas permeability was measured at 18°C, 40% RH, using Mocon instruments.

COMPARISON EXAMPLE 1

[0064] The preparation of example 1 was repeated, the only difference being that a mixture with 90/10 by weight of COPET (containing 2% IPA, with IV = 0.8 dl/g) and of poly MXD-6, not containing PMDA, was extruded.

[0065] 1.5-liter bottles were prepared by injection-blow molding in the conditions used in examples 6-7.

[0066] The permeability to O_2 and CO_2 of the bottles was much higher than in the bottles of examples 6-7.

COMPARISON EXAMPLE 2

[0067] 1.5-liter bottles were prepared in the conditions of examples 6-7, using a resin formed by COPET with 2% IPA and IV=0.8 dl/g.

[0068] The data on O_2 and CO_2 permeability are listed in table 1.

[0069] The disclosures in Italian Patent Application No. MI98A001335 from which this application claims priority are incorporated herein by reference.

TABLE 1

MIXTURES

	Comparison 2	Example 1	Example 2	Example 3	Example 4
% weight pMXD-6	0	10	10	10	70
% IPA	2	4.5	10	2	4.5
O_2 permeability					
1.5-liter bottles ml/bott/d/atm	0.53	0.13	0.1	0.12	
2-liter bottles	0.62	0.23	0.14	0.14	
CO_2 permeability					
1.5-liter bottles ml/bott/d/atm	18.2	7.25	5.31	7.02	2.7
Improvement %					
O_2 permeability					
1.5-liter bottles		407	550	449	
2-liter bottles		362	578	567	
CO_2 permeability					
1.5-liter bottles		251	343	250	670

Claims

1. A polymeric material suitable for preparing biaxially-oriented films and containers having high characteristics of

resistance to gas permeability, obtained by mixing a melted material under such conditions that the polymeric components thereof are rheologically compatible, comprising:

a) an aromatic polyester resin, premixed with a dianhydride of a tetracarboxylic acid, in an amount between 0.01 and 3% by weight;
b) a polyamide derived from m-xylylene diamine and from a dicarboxylic acid with 6-22 carbon atoms in an amount equal to 1 to 90% by weight on the sum of a) + b).

2. A material according to claim 1, wherein the polyester resin is copolyethylene terephthalate containing up to 25% of units derived from isophthalic acid.

3. A material according to claims 1-2, wherein the polyamide is poly m-xylylene adipamide.

4. A polymeric material according to claims 1-3, wherein the dianhydride is pyromellitic dianhydride.

5. A polymeric material according to claims 1-4, wherein the material obtained from the melted mixture comprising the components a) and b) is subjected to solid-state polycondensation until the intrinsic viscosity of the starting polyester is increased of at least 0.1 units.

6. A polymeric material according to claim 5, wherein the polyester premixed with the dianhydride is subjected to solid-state polycondensation until the intrinsic viscosity of the initial polyester is increased of at least 0.1 units.

7. A polymeric material according to claims 1-6, wherein the polyester and the polyamide have melt viscosities, at the mixing temperature, in a ratio from 0.2:1 to 4:1.

8. A polymeric material according to claims 1-7, capable of providing containers whose resistance to oxygen permeability is less than 0.065 ml/bottle/day/atm, measured on a 1.5-liter bottle with a thickness of 225 microns prepared by injection-blow molding.

9. A polymeric material comprising an aromatic polyester resin and a polyamide derived from dicarboxylic acid and an arilene diamine, wherein the polyamide is dispersed in a polyester resin matrix with average size of the dispersed domains of less than 1 micron.

10. A polymeric material according to claim 9 wherein the average size of the dispersed domains is from 0.2 to 0.4 micron.

11. A polymeric material according to claims 9-10 wherein the polyester resin is a copolyethylene terephthalate containing up to 25% of units derived from isophthalic acid and the polyamide is poly-m-xylylene adipamide.

12. Biaxially-oriented films and containers obtained from the polymeric material of claims 1-11.

13. Containers according to claim 12, in the form of bottles for carbonated beverages.

14. Containers according to claims 12-13, obtained by injection blow-molding.

15. Containers according to claims 12-14, wherein the aromatic polyester is copolyethylene terephthalate containing up to 25% units or sequences derived from isophthalic acid.

16. Containers and films according to claims 12-15, wherein the polyamide is poly m-xylylene adipamide.

17. Containers and films according to claims 12-16, wherein the dianhydride of the tetracarboxylic acid is pyromellitic dianhydride.

18. Containers and films according to claims 12-17, wherein the starting polyester of the material used to prepare the container has an intrinsic viscosity from 0.3 to 0.8 dl/g.

19. Containers and films according to claims 12-18, wherein the material obtained from the melted mixture comprising the polyester, the polyamide and the dianhydride is subjected to solid-state polycondensation for a time and tem-

perature conditions sufficient to increase the intrinsic viscosity of the polyester by at least 0.1 units.

20. Containers and films according to claims 12-19, wherein the polyester premixed with the dianhydride is subjected to a solid-state polycondensation treatment so as to increase by 0.1 units the intrinsic viscosity of the initial polyester.

21. Containers and films according to claims 12-20, wherein the melt viscosities of the polyester and the polyamide, determined at the mixing temperature, are in a ratio from 0.2:1 to 4:1.

22. Containers and films according to claims 12-21, wherein the mixing of the components is performed in the extruder.

23. Containers and films according to claims 12-22 **characterized in that** they have an oxygen permeability of less than 0.065 ml/bottle/day/atm, measured on a 1.5-liter bottle with a thickness of 225 microns obtained by injection blow molding.

24. Films according to the preceding claims 15-22, obtained by biaxial stretching of films prepared by cast-extrusion.

25. Films according to the preceding claims 15-22, obtained by blow-molding using the double-bubble method.

Patentansprüche

1. Zur Herstellung von biaxial orientierten Folien und Behältern mit hoher Gasundurchlässigkeit geeignetes polymeres Material, das durch Mischen eines schmelzflüssigen Materials, das:

   a) ein mit einem Tetracarbonsäuredianhydrid vorgemischtes aromatisches Polyesterharz in einer Menge zwischen 0,01 und 3 Gew.-%,

   b) ein von m-Xylylendiamin und einer Dicarbonsäure mit 6-22 Kohlenstoffatomen abgeleitetes Polyamid in einer Menge von 1 bis 90 Gew.-%, bezogen auf die Summe von a) + b),

   enthält, unter solchen Bedingungen, daß die polymeren Komponenten davon rheologisch verträglich sind, erhalten wird.

2. Material nach Anspruch 1, bei dem es sich bei dem Polyesterharz um Copolyethylenterephthalat mit bis zu 25% von Isophthalsäure abgeleiteten Einheiten handelt.

3. Material nach den Ansprüchen 1-2, bei dem es sich bei dem Polyamid um Poly-m-xylylenadipamid handelt.

4. Polymeres Material nach den Ansprüchen 1-3, bei dem es sich bei dem Dianhydrid um Pyromellitsäuredianhydrid handelt.

5. Polymeres Material nach den Ansprüchen 1-4, bei dem das aus der die Komponenten a) und b) enthaltenden schmelzflüssigen Mischung erhaltene Material einer Festphasenpolykondensation unterworfen wird, bis die intrinsische Viskosität des Ausgangspolyesters um mindestens 0,1 Einheiten zugenommen hat.

6. Polymeres Material nach Anspruch 5, bei dem der mit dem Dianhydrid vorgemischte Polyester einer Festphasenpolykondensation unterworfen wird, bis die intrinsische Viskosität des Ausgangspolyesters um mindestens 0,1 Einheiten zugenommen hat.

7. Polymeres Material nach den Ansprüchen 1-6, bei dem der Polyester und das Polyamid Schmelzeviskositäten bei der. Mischtemperatur in einem Verhältnis von 0,2:1 bis 4:1 aufweisen.

8. Polymeres Material nach den Ansprüchen 1-7, das zur Bereitstellung von Behältern geeignet ist, deren an einer durch Spritzblasformen hergestellten 1,5-Liter-Flasche mit einer Dicke von 225 Mikron bestimmte Sauerstoffdurchlässigkeit weniger als 0,065 ml/Flasche/Tag/atm beträgt.

9. Polymeres Material, das ein aromatisches Polyesterharz und ein von einer Dicarbonsäure und einem Arylendiamin

abgeleitetes Polyamid enthält, bei dem das Polyamid in einer Polymerharzmatrix dispergiert ist, wobei die durchschnittliche Größe der dispergierten Domänen weniger als 1 Mikron beträgt.

10. Polymeres Material nach Anspruch 9, bei dem die durchschnittliche Größe der dispergierten Domänen 0,2 bis 0,4 Mikron beträgt.

11. Polymeres Material nach den Ansprüchen 9-10, bei dem es sich bei dem Polyesterharz um Copolyethylenterephthalat mit bis zu 25% von Isophthalsäure abgeleiteten Einheiten und bei dem Polyamid um Poly-m-xylylenadipamid handelt.

12. Aus dem polymeren Material nach den Ansprüchen 1-11 erhaltene biaxial orientierte Folien und Behälter.

13. Behälter nach Anspruch 12 in Form von Flaschen für kohlensäurehaltige Getränke.

14. Durch Spritzblasformen erhaltene Behälter nach den Ansprüchen 12-13.

15. Behälter nach den Ansprüchen 12-14, bei denen es sich bei dem aromatischen Polyester um Copolyethylenterephthalat mit bis zu 25% von Isophthalsäure abgeleiteten Einheiten oder Sequenzen handelt.

16. Behälter und Folien nach den Ansprüchen 12-15, bei denen es sich bei dem Polyamid um Poly-m-xylylenadipamid handelt.

17. Behälter und Folien nach den Ansprüchen 12-16, bei denen es sich bei dem Tetracarbonsäuredianhydrid um Pyromellitsäuredianhydrid handelt.

18. Behälter und Folien nach den Ansprüchen 12-17, bei denen der zur Herstellung des Behälters verwendete Ausgangspolyester, eine intrinsische Viskosität von 0,3 bis 0,8 dl/g aufweist.

19. Behälter und Folien nach den Ansprüchen 12-18, bei denen das aus der den Polyester, das Polyamid und das Dianhydrid enthaltenden schmelzflüssigen Mischung erhaltene Material einer Festphasenpolykondensation über einen solchen Zeitraum und unter solchen Temperaturbedingungen unterworfen wird, daß die intrinsische Viskosität des Polyesters um mindestens 0,1 Einheiten erhöht wird.

20. Behälter und Folien nach den Ansprüchen 12-19, bei denen der mit dem Dianhydrid vorgemischte Polyester einer Festphasenpolykondensation zur Erhöhung der intrinsischen Viskosität des Ausgangspolyesters um mindestens 0,1 Einheiten unterworfen wird.

21. Behälter und Folien nach den Ansprüchen 12-20, bei denen die bei der Mischtemperatur bestimmten Schmelzeviskositäten des Polyesters und des Polyamids ein Verhältnis von 0,2:1 bis 4:1 aufweisen.

22. Behälter und Folien nach den Ansprüchen 12-21, bei denen das Mischen der Komponenten in einem Extruder durchgeführt wird.

23. Behälter und Folien nach den Ansprüchen 12-22, **dadurch gekennzeichnet, daß** sie eine an einer durch Spritzblasformen hergestellten 1,5-Liter-Flasche mit einer Dicke von 225 Mikron bestimmte Sauerstoffdurchlässigkeit von weniger als 0,065 ml/Flasche/Tag/atm aufweisen.

24. Folien nach den vorhergehenden Ansprüchen 15-22, die durch biaxiales Strecken von durch Flachfolienextrusion hergestellten Folien erhalten werden.

25. Folien nach den vorhergehenden Ansprüchen 15-22, die durch Blasformen nach dem Double-Bubble-Verfahren erhalten werden.

Revendications

1. Matière polymère appropriée à la préparation de films et de conteneurs orientés biaxialement et ayant des caractéristiques élevées de résistance à la perméabilité aux gaz, obtenue par mélange d'une matière fondue dans des

conditions telles que les composants polymères de celle-ci sont compatibles du point de vue rhéologique, comprenant :

a) une résine de polyester aromatique, prémélangée avec un dianhydride d'un acide tétracarboxylique, en une quantité comprise entre 0,01 et 3 % en poids ;
b) un polyamide dérivé de m-xylylènediamine et d'un acide dicarboxylique ayant 6-22 atomes de carbone, en une quantité égale à 1 à 90 % en poids de la somme de a) + b).

2. Matière selon la revendication 1, dans laquelle la résine de polyester est du téréphtalate de copolyéthylène contenant jusqu'à 25 % d'unités dérivées de l'acide isophtalique.

3. Matière selon les revendications 1-2, dans laquelle le polyamide est du poly-m-xylylène-adipamide.

4. Matière polymère selon les revendications 1-3, dans laquelle le dianhydride est du dianhydride pyromellique.

5. Matière polymère selon les revendications 1-4, dans laquelle la matière obtenue à partir du mélange fondu comprenant les composants a) et b) est soumise à une polycondensation à l'état solide jusqu'à ce que la viscosité intrinsèque du polyester de départ soit augmentée d'au moins 0,1 unité.

6. Matière polymère selon la revendication 5, dans laquelle le polyester prémélangé avec le dianhydride est soumis à une polycondensation à l'état solide jusqu'à ce que la viscosité intrinsèque du polyester initial soit augmentée d'au moins 0,1 unité.

7. Matière polymère selon les revendications 1-6, dans laquelle le polyester et le polyamide ont des viscosités à l'état fondu, à la température de mélange, dans un rapport de 0,2:1 à 4:1.

8. Matière polymère selon les revendications 1-7, capable de fournir des conteneurs dont la résistance à la perméabilité à l'oxygène est inférieure à 0,065 ml/bouteille/jour/atm, mesurée sur une bouteille de 1,5 litre ayant une épaisseur de 225 micromètres et préparée par moulage par injection-soufflage.

9. Matière polymère comprenant une résine de polyester aromatique et un polyamide dérivé d'un acide dicarboxylique et d'une arylènediamine, dans laquelle le polyamide est dispersé dans une matrice de résine de polyester avec une taille moyenne des domaines dispersés inférieure à 1 micromètre.

10. Matière polymère selon la revendication 9, dans laquelle la taille moyenne des domaines dispersés est de 0,2 à 0,4 micromètre.

11. Matière polymère selon les revendications 9-10, dans laquelle la résine de polyester est un téréphtalate de copolyéthylène contenant jusqu'à 25 % d'unités dérivées de l'acide isophtalique, et le polyamide est du poly-m-xylylène-adipamide.

12. Films et conteneurs orientés biaxialement obtenus à partir de la matière polymère selon les revendications 1-11.

13. Conteneurs selon la revendication 12, sous la forme de bouteilles pour boissons gazeuses.

14. Conteneurs selon les revendications 12-13, obtenus par moulage par injection-soufflage.

15. Conteneurs selon les revendications 12-14, dans lesquels le polyester aromatique est du téréphtalate de copolyéthylène contenant jusqu'à 25 % d'unités ou de séquences dérivées de l'acide isophtalique.

16. Conteneurs et films selon les revendications 12-15, dans lesquels le polyamide est du poly-m-xylylène-adipamide.

17. Conteneurs et films selon les revendications 12-16, dans lesquels le dianhydride de l'acide tétracarboxylique est du dianhydride pyromellique.

18. Conteneurs et films selon les revendications 12-17, dans lesquels le polyester de départ de la matière utilisée pour préparer le conteneur a une viscosité intrinsèque de 0,3 à 0,8 dl/g.

19. Conteneurs et films selon les revendications 12-18, dans lesquels la matière obtenue à partir du mélange fondu comprenant le polyester, le polyamide et le dianhydride est soumise à une polycondensation à l'état solide dans des conditions de temps et de température suffisantes pour augmenter la viscosité intrinsèque du polyester d'au moins 0,1 unité.

20. Conteneurs et films selon les revendications 12-19, dans lesquels le polyester prémélangé avec le dianhydride est soumis à un traitement de polycondensation à l'état solide de façon à augmenter de 0,1 unité la viscosité intrinsèque du polyester initial.

21. Conteneurs et films selon les revendications 12-20, dans lesquels les viscosités à l'état fondu du polyester et du polyamide, déterminées à la température de mélange, sont dans un rapport de 0,2:1 à 4:1.

22. Conteneurs et films selon les revendications 12-21, dans lesquels le mélange des composants est effectué dans l'extrudeuse.

23. Conteneurs et films selon les revendications 12-22, **caractérisés en ce qu**'ils ont une perméabilité à l'oxygène inférieure à 0, 065 ml/bouteille/jour/atm, mesurée sur une bouteille de 1,5 litre ayant une épaisseur de 225 micromètres obtenue par moulage par injection-soufflage.

24. Films selon les revendications 15-22 précédentes, obtenus par étirage biaxial de films préparés par extrusion-coulée.

25. Films selon les revendications 15-22 précédentes, obtenus par moulage par soufflage en utilisant le procédé à double bulle.